

## CROSSLINKED CELLULOSIC PRODUCT FORMED BY EXTRUSION PROCESS

## CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of the priority of the filing date of U.S. Patent Application No. 60/248,520, filed November 14, 2000, which is expressly incorporated herein by reference in its entirety.

## FIELD OF THE INVENTION

The present invention relates generally to a cellulosic fibrous product and, more particularly, to a crosslinked cellulosic fibrous product formed by an extrusion process.

## BACKGROUND OF THE INVENTION

Crosslinked cellulosic fibers are advantageously incorporated into a variety of fibrous products to enhance product bulk, resilience, and dryness. Absorbent articles, such as diapers, are typically formed from fibrous composites that include absorbent fibers such as wood pulp fibers, and can additionally include crosslinked cellulosic fibers. When incorporated into absorbent articles, such fibrous composites can provide a product that offers the advantages of high liquid acquisition rate and high liquid wicking capacity imparted by the crosslinked fibers and absorbent fibers, respectively. However, fibrous composites that include relatively high percentages of crosslinked fibers suffer from low sheet strength.

The relatively low strength of sheets that include crosslinked fibers is due in part to the loss of hydrogen bonding sites that accompanies cellulose crosslinking. As a result of their chemical modification, crosslinked cellulosic fibers have fewer hydroxyl groups that are available for forming hydrogen bonds between fibers. The

lower tendency of crosslinked fibers to form interfiber bonds generally precludes their formation into sheets or webs having any significant structural integrity.

Historically, cellulose structures have been formed from water based sheet forming processes. Over time, airlaid and foam-forming processes were developed to use new materials and impart improved properties of the resulting web. Foam-forming processes showed improved capability to utilize long fibers of natural or synthetic origin and provided a bulky web. Airlaid processes provided bulk and softness but limited strength without a high binder content. Crosslinked fibers have been used in the above mentioned processes to improve web properties such as resilience, bulk and acquisition. Crosslinked fibers have previously only been available as individually crosslinked fibers packaged in a bale. Numerous patents speak of processes to make and to use individually crosslinked fibers. Therefore there is a need to develop a process that eliminates the step of individually crosslinking the cellulose fibers.

Personal care absorbent products, for example, infant diapers, adult incontinence products, and feminine care products, include liquid acquisition and/or distribution layers that serve to rapidly acquire and then distribute acquired liquid to a storage core for retention. To achieve rapid acquisition and distribution, these layers may include crosslinked cellulosic fibers, which impart bulk and resilience to the layers. However, as noted above, webs that include high proportions of crosslinked fibers suffer from a lack of structural integrity. The problem of loss of structural integrity is traditionally addressed by sandwiching webs that include crosslinked fibers between either tissues and nonwoven sheets and secured with an adhesive. Such structures are required to seek to maintain web integrity.

Accordingly, there exists a need for a cellulosic web that possesses the advantageous properties of webs that include crosslinked cellulosic fibers and yet further advantageously maintains its structural integrity. The present invention seeks to fulfill these needs and provides further related advantages.

#### SUMMARY OF THE INVENTION

In one aspect, the present invention provides a crosslinked cellulosic fibrous product that includes in situ crosslinked cellulosic fibers. In one embodiment, the product further includes a bonding agent. The product can optionally include other fibers alone, absorbent materials alone, and other fibers and absorbent materials.

In another aspect of the invention, methods for forming the crosslinked cellulosic fibrous product is provided. In one embodiment, the product is formed using a screw extrusion device. In another embodiment, the product is formed using a rotary mixing extrusion device.

In a further aspect, the present invention provides absorbent articles that include the bonded cellulosic fibrous product. The product can be combined with one or more other layers to provide structures that can be incorporated into absorbent articles such as infant diapers, adult incontinence products, and feminine care products.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing aspects and many of the attendant advantages of this invention will become more readily appreciated as the same become better understood by reference to the following detailed description, when taken in conjunction with the accompanying drawings, wherein:

FIGURE 1 is a graph illustrating liquid drainage from foam as a function of time for foams having densities of 137g/L, 95g/L, 66g/L, and 41g/L, respectively;

FIGURE 2 is a flow diagram illustrating a representative method for making an extruded composite in accordance with the present invention;

FIGURE 3A is an image of a representative mixing device useful in the method of the present invention;

FIGURE 3B is an image of the stator of the mixing device illustrated in FIGURE 3A;

FIGURE 3C is an image of the mixing device of FIGURE 3A with the rotor removed;

FIGURE 4 is a schematic illustration of a representative extrusion device useful in the present invention illustrating positions at which various materials may be added;

FIGURE 5 is a graph comparing the density of fibrous composites made from (a) southern pine fibers and (b) fibers crosslinked with a blend of citric and polyacrylic acids by four methods: foam laid, airlaid, wetlaid, and the extrusion process of the invention;

FIGURE 6 is a graph illustrating pore size distribution for a representative extruded composite formed in accordance with the present invention that includes cellulose fibers crosslinked with a blend of polyacrylic and citric acids (13% by weight crosslinked based on fiber);

5        FIGURE 7 is a graph illustrating pore size distribution for a representative foam laid composite that includes cellulose fibers crosslinked with a blend of polyacrylic and citric acids;

FIGURE 8 is a graph illustrating pore size distribution for a representative airlaid composite that includes cellulose fibers crosslinked with a blend of polyacrylic and citric acids;

10       FIGURE 9 is a graph illustrating pore size distribution for a representative wetlaid composite that includes cellulose fibers crosslinked with a blend of polyacrylic and citric acids;

FIGURE 10 is a graph illustrating absorption and desorption curves obtained using an autoporosimeter for an airlaid composite that includes southern pine fibers;

15       FIGURE 11 is a graph that compares the mid-point desorption pressure (MDP) of representative extruded composites formed in accordance with the present invention ("pine fiber" refers to a composite that includes southern pine fibers, "pre-crosslinked Chemistry B composite" refers to a composite that includes citric acid crosslinked fibers, and "in situ Chemistry B composite" refers to a composite that includes cellulose fibers treated with citric acid and cured in the composite);

FIGURE 12 is a graph illustrating the effect on crosslinking chemistry on the mid-point desorption pressure for representative extruded composites formed in accordance with the present invention ("pre-crosslinked Chemistry A" refers to a composite that includes cellulose fibers crosslinked with a blend of polyacrylic and citric acids, "pre-crosslinked Chemistry B" refers to a composite that includes citric acid crosslinked fibers, "in situ Chemistry B" refers to a composite that includes cellulose fibers that had been treated with citric acid and cured in the composite, and in situ Chemistry C" refers to a composite that includes cellulose fibers treated with polyacrylic acid and cured in the composite);

30       FIGURE 13 is a graph illustrating the effect of latex content on the mid-point desorption pressure as a function of crosslinking chemistry for representative extruded

composites formed in accordance with the present invention ("pre-crosslinked Chemistry B" refers to a composite that includes citric acid crosslinked fibers, "pre-crosslinked Chemistry B plus 5 percent latex" refers to a composite that includes citric acid crosslinked fibers and 5 percent by weight latex, "in situ Chemistry B" refers to a composite that includes fibers treated with citric acid and cured in the composite, and "in situ Chemistry B plus 5 percent latex" refers to a composite that includes fibers treated with citric acid and cured in the composite and 5 percent by weight latex);

FIGURE 14 is a graph illustrating the effect of in situ crosslinking on the tensile strength of representative extruded composites formed in accordance with the present invention that include citric acid crosslinked fibers and polyacrylic acid crosslinked fibers ("2 percent in situ" refers to a composite that includes fibers treated with 2 percent by weight crosslinking agent, "6 percent in situ" refers to a composite that includes fibers treated with 6 percent by weight crosslinking agent, and "6 percent pre-crosslinked" refers to a composite that includes fibers crosslinked with 6 percent by weight crosslinking agent);

FIGURE 15 is a graph illustrating the effect of latex and fiber type on the strength of representative composites formed in accordance with the present invention ("pine" refers to a composite that includes southern pine fibers, "blend" refers to a composite that includes a 50/50 blend of southern pine fibers and fibers crosslinked with a blend of polyacrylic and citric acids, and "Chemistry A" refers to a composite that includes fibers crosslinked with a blend of polyacrylic and citric acids);

FIGURE 16 is a graph illustrating the effect of in situ crosslinking chemistry and latex on the tensile strength of representative extruded composites formed in accordance with the present invention ("Chem B" refers to a composite that includes citric acid crosslinked fibers and "Chem C" refers to a composite that includes polyacrylic acid crosslinked fibers);

FIGURE 17 is a graph illustrating pore size distribution for a foam laid composite;

FIGURE 18 is a graph illustrating the mid-point desorption pressure for the composite of FIGURE 17;

FIGURE 19 is a graph illustrating pore size distribution for a foam laid composite;

FIGURE 20 is a graph illustrating the mid-point desorption pressure for the composite of FIGURE 19;

FIGURE 21 is a graph illustrating the pore size distribution for a representative composite formed in accordance with the present invention (a composite including southern pine fibers);

FIGURE 22 is a graph illustrating the mid-point desorption pressure for the composite of FIGURE 21;

FIGURE 23 is a graph illustrating pore size distribution for a representative extruded composite formed in accordance with the present invention ( a composite including southern pine fibers and 5 percent latex);

FIGURE 24 is a graph illustrating pore size distribution for a representative extruded composite of the present invention (a composite including fibers crosslinked with a blend of citric and polyacrylic acids with 5 percent latex);

FIGURE 25 is a graph illustrating pore size distribution for a representative extruded composite of the present invention (a composite including a 50:50 blend of southern pine fibers and fibers crosslinked with a blend of citric and polyacrylic acids with 5 percent latex);

FIGURE 26 is a graph illustrating the fourth gush acquisition rate of representative extruded composites formed in accordance with the present invention compared to control composites;

FIGURE 27 is a graph illustrating the mid-point desorption pressure for a representative extruded composite formed in accordance with the present invention (a composite that includes a blend of citric and polyacrylic acid crosslinked fibers with 15 percent latex);

FIGURES 28 is a graph illustrating the mid-point desorption pressure for a representative extruded composite formed in accordance with the present invention (a composite that includes a blend of citric and polyacrylic acid crosslinked fibers )

FIGURE 29 is a graph illustrating the mid-point desorption pressure for a foam laid composite;

FIGURE 30 is a graph illustrating the mid-point desorption pressure for a wetlaid composite; and

FIGURE 31 is a graph illustrating the mean desorption pressure for airlaid composites.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In one aspect, the present invention provides a bonded cellulosic fibrous product that includes in situ crosslinked cellulosic fibers. As used herein, the term "in situ crosslinked cellulosic fibers", refers to cellulosic fibers that have been crosslinked during the formation of the web. Therefore, the product of the invention is distinguished from conventional webs that include crosslinked cellulosic fibers that are first formed and then introduced to the web during the web formation process.

The product includes in situ crosslinked cellulosic fibers. Because the fibers are crosslinked during the web formation process (i.e., in situ), the product includes intrafiber crosslinked cellulosic fibers (i.e., fibers having crosslinks within each fiber) and interfiber crosslinked cellulosic fibers (i.e., fibers having crosslinks between fibers). The product has a bonded structure and includes intrafiber crosslinked cellulosic fibers that are further crosslinked to adjacent fibers through interfiber crosslinks. The product possesses the advantageous properties of bulk and resiliency associated with intrafiber crosslinked fibers and the advantage of structural integrity imparted to the structure by the bonding between fibers. The product is a bonded web in which the crosslinked fibers and the bonded structure of the web itself contribute to the resiliency and liquid acquisition performance of the web.

In one embodiment, the product can be produced by (1) forming a web of cellulosic fibers, at least some of which having been treated with a crosslinking agent and, if necessary, crosslinking catalyst; (2) drying the web; and (3) heating the web at a temperature and for a time sufficient to effect crosslinking.

Suitable fibers useful in forming the product of the invention include cellulosic fibers that have been treated with a crosslinking agent and, if necessary, crosslinking catalyst and then dried without curing the crosslinking agent. These dried and treated fibers can be introduced into the forming device for subsequent product formation.

Any one of a number of crosslinking agents and crosslinking catalysts, if necessary, can be used to provide the product of the invention. The following is a representative list of useful crosslinking agents and catalysts. Each of the patents noted below is expressly incorporated herein by reference in its entirety.

Suitable urea-based crosslinking agents include substituted ureas such as methyolated ureas, methyolated cyclic ureas, methyolated lower alkyl cyclic ureas, methyolated dihydroxy cyclic ureas, dihydroxy cyclic ureas, and lower alkyl substituted cyclic ureas. Specific urea-based crosslinking agents include

5 dimethyldihydroxy urea (DMDHU, 1,3-dimethyl-4,5-dihydroxy-2-imidazolidinone), dimethyloldihydroxyethylene urea (DMDHEU, 1,3-dihydroxymethyl-4,5-dihydroxy-2-imidazolidinone), dimethylol urea (DMU, bis[N-hydroxymethyl]urea), dihydroxyethylene urea (DHEU, 4,5-dihydroxy-2-imidazolidinone), dimethylolethylene urea (DMEU, 1,3-dihydroxymethyl-2-imidazolidinone), and

10 dimethyldihydroxyethylene urea (DDI, 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone).

Suitable crosslinking agents include dialdehydes such as C<sub>2</sub>-C<sub>8</sub> dialdehydes (e.g., glyoxal), C<sub>2</sub>-C<sub>8</sub> dialdehyde acid analogs having at least one aldehyde group, and oligomers of these aldehyde and dialdehyde acid analogs, as described in U.S. Patents

15 Nos. 4,822,453; 4,888,093; 4,889,595; 4,889,596; 4,889,597; and 4,898,642. Other suitable dialdehyde crosslinking agents include those described in U.S. Patents Nos. 4,853,086; 4,900,324; and 5,843,061.

Other suitable crosslinking agents include aldehyde and urea-based formaldehyde addition products. See, for example, U.S. Patents Nos. 3,224,926;

20 3,241,533; 3,932,209; 4,035,147; 3,756,913; 4,689,118; 4,822,453; 3,440,135; 4,935,022; 3,819,470; and 3,658,613.

Suitable crosslinking agents include glyoxal adducts of ureas, for example, U.S. Patent No. 4,968,774, and glyoxal/cyclic urea adducts as described in U.S. Patents Nos. 4,285,690; 4,332,586; 4,396,391; 4,455,416; and 4,505,712.

25 Other suitable crosslinking agents include carboxylic acid crosslinking agents such as polycarboxylic acids. Polycarboxylic acid crosslinking agents (e.g., citric acid, propane tricarboxylic acid, and butane tetracarboxylic acid) and catalysts are described in U.S. Patents Nos. 3,526,048; 4,820,307; 4,936,865; 4,975,209; and 5,221,285. The use of C<sub>2</sub>-C<sub>9</sub> polycarboxylic acids that contain at least three carboxyl groups (e.g.,

30 citric acid and oxydisuccinic acid) as crosslinking agents is described in U.S. Patents Nos. 5,137,537; 5,183,707; 5,190,563; 5,562,740, and 5,873,979.

Polymeric polycarboxylic acids are also suitable crosslinking agents. Suitable polymeric polycarboxylic acid crosslinking agents are described in U.S. Patents Nos. 4,391,878; 4,420,368; 4,431,481; 5,049,235; 5,160,789; 5,442,899; 5,698,074; 5,496,476; 5,496,477; 5,728,771; 5,705,475; and 5,981,739. Polyacrylic acid and related copolymers as crosslinking agents are described U.S. Patents Nos. 6,306,251; 5,549,791; and 5,998,511. Polymaleic acid crosslinking agents are described in U.S. Patent No. 5,998,511.

Specific suitable polycarboxylic acid crosslinking agents include citric acid, tartaric acid, malic acid, succinic acid, glutaric acid, citraconic acid, itaconic acid, tartrate monosuccinic acid, maleic acid, polyacrylic acid, polymethacrylic acid, polymaleic acid, polymethylvinylether-co-maleate copolymer, polymethylvinylether-co-itaconate copolymer, copolymers of acrylic acid, and copolymers of maleic acid.

Other suitable crosslinking agents are described in U.S. Patents Nos. 5,225,047; 5,366,591; 5,556,976; and 5,536,369.

Suitable catalysts can include acidic salts, such as ammonium chloride, ammonium sulfate, aluminum chloride, magnesium chloride, magnesium nitrate, and alkali metal salts of phosphorous-containing acids. In one embodiment, the crosslinking catalyst is sodium hypophosphite.

Mixtures or blends of crosslinking agents and catalysts can also be used.

The crosslinking agent is applied to the cellulosic fibers in an amount sufficient to effect intrafiber crosslinking and interfiber crosslinking as described above. The amount applied to the cellulosic fibers can be from about 1 to about 10 percent by weight based on the total weight of fibers. In one embodiment, crosslinking agent in an amount from about 4 to about 6 percent by weight based on the total weight of fibers.

Suitable cellulosic fibers for forming the product of the invention include those known to those skilled in the art and include any fiber or fibrous mixture that can be crosslinked and from which a fibrous web or sheet can be formed.

Although available from other sources, cellulosic fibers are derived primarily from wood pulp. Suitable wood pulp fibers for use with the invention can be obtained from well-known chemical processes such as the kraft and sulfite processes, with or without subsequent bleaching. Pulp fibers can also be processed by

thermomechanical, chemithermomechanical methods, or combinations thereof. The preferred pulp fiber is produced by chemical methods. Groundwood fibers, recycled or secondary wood pulp fibers, and bleached and unbleached wood pulp fibers can be used. Softwoods and hardwoods can be used. Details of the selection of wood pulp fibers are well known to those skilled in the art. These fibers are commercially available from a number of companies, including Weyerhaeuser Company, the assignee of the present invention. For example, suitable cellulose fibers produced from southern pine that are usable with the present invention are available from Weyerhaeuser Company under the designations CF416, NF405, PL416, FR516, and NB416.

The wood pulp fibers useful in the present invention can also be pretreated prior to use. This pretreatment may include physical treatment, such as subjecting the fibers to steam, or chemical treatment.

Although not to be construed as a limitation, examples of pretreating fibers include the application of surfactants or other liquids, which modify the surface chemistry of the fibers. Other pretreatments include incorporation of antimicrobials, pigments, dyes and densification or softening agents. Fibers pretreated with other chemicals, such as thermoplastic and thermosetting resins also may be used. Combinations of pretreatments also may be employed. Similar treatments can also be applied after formation of the fibrous product in post-treatment processes.

Cellulosic fibers treated with particle binders and/or densification/softness aids known in the art can also be employed in accordance with the present invention. The particle binders serve to attach other materials, such as superabsorbent polymers, as well as others, to the cellulosic fibers. Cellulosic fibers treated with suitable particle binders and/or densification/softness aids and the process for combining them with cellulose fibers are disclosed in the following U.S. patents: (1) Patent No. 5,543,215, entitled "Polymeric Binders for Binding Particles to Fibers"; (2) Patent No. 5,538,783, entitled "Non-Polymeric Organic Binders for Binding Particles to Fibers"; (3) Patent No. 5,300,192, entitled "Wet Laid Fiber Sheet Manufacturing With Reactivable Binders for Binding Particles to Binders"; (4) Patent No. 5,352,480, entitled "Method for Binding Particles to Fibers Using Reactivable Binders"; (5) Patent No. 5,308,896, entitled "Particle Binders for High-Bulk Fibers"; (6) Patent No. 5,589,256, entitled

"Particle Binders that Enhance Fiber Densification"; (7) Patent No. 5,672,418, entitled "Particle Binders"; (8) Patent No. 5,607,759, entitled "Particle Binding to Fibers"; (9) Patent No. 5,693,411, entitled "Binders for Binding Water Soluble Particles to Fibers"; (10) Patent No. 5,547,745, entitled "Particle Binders"; (11) Patent No. 5,641,561, entitled "Particle Binding to Fibers"; (12) Patent No. 5,308,896, entitled "Particle Binders for High-Bulk Fibers"; (13) Patent No. 5,498,478, entitled "Polyethylene Glycol as a Binder Material for Fibers"; (14) Patent No. 5,609,727, entitled "Fibrous Product for Binding Particles"; (15) Patent No. 5,571,618, entitled "Reactivatable Binders for Binding Particles to Fibers"; (16) Patent No. 5,447,977, entitled "Particle Binders for High Bulk Fibers"; (17) Patent No. 5,614, 570, entitled "Absorbent Articles Containing Binder Carrying High Bulk Fibers"; (18) Patent No. 5,789,326, entitled "Binder Treated Fibers"; and (19) Patent No. 5,611,885, entitled "Particle Binders", each expressly incorporated herein by reference.

In addition to natural fibers, synthetic fibers including polymeric fibers, such as polyolefin, polyamide, polyester, polyvinyl alcohol, polyvinyl acetate fibers, can also be incorporated into the product. Suitable synthetic fibers include, for example, polyethylene terephthalate, polyethylene, polypropylene, nylon, and rayon fibers. Other suitable synthetic fibers include those made from thermoplastic polymers, cellulosic and other fibers coated with thermoplastic polymers, and multicomponent fibers in which at least one of the components includes a thermoplastic polymer. Single and multicomponent fibers can be manufactured from polyester, polyethylene, polypropylene, and other conventional thermoplastic fibrous materials. Single and multicomponent fibers are commercially available. Suitable bicomponent fibers include CELBOND fibers available from Hoechst-Celanese Company. The product can also include combinations of natural and synthetic fibers.

In one embodiment, the product further includes a bonding agent. The bonding agent serves to further enhance the structural integrity of the product. Suitable bonding agents include thermoplastic materials, such as bicomponent fibers and latexes, and wet strength agents. When the bonding agent is a thermoplastic fiber, the fiber can be combined with cellulosic fibers and then formed into the web to be treated with the crosslinking agent. When the bonding agent is a wet strength agent, the

bonding agent can be applied to the web prior to subjecting the web to fiber crosslinking conditions.

Suitable thermoplastic fibers include cellulosic and other fibers coated with thermoplastic polymers, and multicomponent fibers in which at least one of the components includes a thermoplastic polymer. Single and multicomponent fibers can be manufactured from polyester, polyethylene, polypropylene, and other conventional thermoplastic fibrous materials. Single and multicomponent fibers are commercially available. Suitable bicomponent fibers include CELBOND fibers available from Hoechst-Celanese Company.

Suitable wet strength agents include cationic modified starch having nitrogen-containing groups (e.g., amino groups) such as those available from National Starch and Chemical Corp., Bridgewater, NJ; latex; wet strength resins, such as polyamide-epichlorohydrin resin (e.g., KYMENE 557LX, Hercules, Inc., Wilmington, DE), and polyacrylamide resin (see, e.g., U.S. Patent No. 3,556,932 and also the commercially available polyacrylamide marketed by American Cyanamid Co., Stamford, CT, under the trade name PAREZ 631 NC); urea formaldehyde and melamine formaldehyde resins; and polyethylenimine resins. A general discussion on wet strength resins utilized in the paper field, and generally applicable in the present invention, can be found in TAPPI monograph series No. 29, "Wet Strength in Paper and Paperboard", Technical Association of the Pulp and Paper Industry (New York, 1965).

In other embodiments, the product can include other fibers. Other fibers include, for example, the cellulosic fibers, particularly the wood pulp fibers described above, as well as hemp, bagasse, cotton, groundwood, bleached and unbleached pulp, recycled or secondary fibers.

For embodiments of the product in which liquid retention is desired, the product can further include absorbent material (e.g., superabsorbent polymer particles). As used herein, the term "absorbent material" refers to a material that absorbs liquid and that generally has an absorbent capacity greater than the cellulosic fibrous component of the composite. Preferably, the absorbent material is a water-swellaable, generally water-insoluble polymeric material capable of absorbing at least about 5, desirably about 20, and preferably about 100 times or more its weight in saline (e.g., 0.9 percent saline). The absorbent material can be swellaable in the dispersion medium



come in a variety of sizes, morphologies, and absorbent properties (available from Clariant under trade designations such as IM 3500 and IM 3900). Other superabsorbent materials are marketed under the trademarks SANWET (supplied by Sanyo Kasei Kogyo Kabushiki Kaisha), and SXM77 (supplied by Stockhausen of Greensboro, North Carolina). Other superabsorbent materials are described in U.S. Patent No. 4,160,059; U.S. Patent No. 4,676,784; U.S. Patent No. 4,673,402; U.S. Patent No. 5,002,814; U.S. Patent No. 5,057,166; U.S. Patent No. 4,102,340; and U.S. Patent No. 4,818,598, all expressly incorporated herein by reference. Products such as diapers that incorporate superabsorbent materials are described in U.S. Patent No. 3,699,103 and U.S. Patent No. 3,670,731.

Suitable superabsorbent materials useful in the product include superabsorbent particles and superabsorbent fibers.

In one embodiment, the product includes a superabsorbent material that swells relatively slowly for the purposes of product manufacturing and yet swells at an acceptable rate so as not to adversely affect the absorbent characteristics of the product or any construct containing the product. Generally, the smaller the absorbent material, the more rapidly the material absorbs liquid.

In another aspect of the invention, methods for forming the bonded cellulosic fibrous product are provided. The bonded cellulosic fibrous product can be formed by an extrusion process.

In general, the methods for forming the product include introducing the components that provide the product into a forming device. Generally, fibers are introduced into the device as a pulp slurry (i.e., a dispersion of fibers in a dispersion medium). The pulp slurry can include dried pulp, never-dried pulp, treated pulp, or mixtures thereof. The pulp slurry can have a relatively high consistency, for example, in one embodiment from about 15 to about 50 percent by weight solids, and in another embodiment from about from about 20 to about 35 percent by weight solids. The pulp introduced into the mixing/extrusion device can then be combined with other components. These components include crosslinking agent and, if necessary, crosslinking catalyst, for embodiments that do not include the introduction of crosslinking agent-treated pulp into the device. For embodiments of the invention that include a bonding agent, the bonding agent can be added to the pulp slurry in the

device. Surfactant and air can also be added to the pulp in the device to provide a foam-forming medium. Other components, such as absorbent material, can be added as necessary to provide the desired product.

5 The product's components are combined and mixed in the device and then extruded from the device. The extruded cellulosic material is then dried and the product ultimately formed by heat treatment. The product has an advantageous low density, as low as about  $0.02 \text{ g/cm}^3$ . Generally, the product has a density in the ranges from about  $0.02$  to about  $0.20 \text{ g/cm}^3$ .

As described above, the product of the invention is formed by subjecting a web  
10 that includes cellulosic fibers to which crosslinking agent and, if necessary, crosslinking catalyst, and bonding agent, if included, to a temperature and for a time sufficient to effect crosslinking (i.e., curing) and fiber bonding. The curing of the crosslinking agent to provide the product can be performed by several methods. Crosslinking typically requires a relatively high temperature ( $180^\circ\text{C}$ ) and long reaction  
15 times (greater than 4 minutes). In one embodiment, the product is formed by heating in a curing oven in which high temperature and large volumes of air are drawn through the web. In another embodiment, curing takes place after the webs have been placed in boxes for shipping. In this embodiment, boxes containing the treated webs are passed through a dryer (e.g., a kiln dryer) to complete the crosslinking reaction.

20 The product of the present invention can be formed as an extended web or sheet that has structural integrity and sheet strength sufficient to permit the fibrous web to be rolled, transported, and used in rolled form in subsequent processes.

The product of the present invention can be supplied in a fibrous rolled form and readily incorporated into subsequent processes. The product can be  
25 advantageously incorporated into a variety of absorbent articles, such as diapers, including disposable diapers and training pants; feminine care products, including sanitary napkins, tampons, and pant liners; adult incontinence products; toweling; surgical and dental sponges; bandages; food tray pads; and the like.

In one embodiment, the process of the invention provides a bonded composite  
30 having intrafiber crosslinked fibers and interfiber crosslinked fibers that impart improved performance of the resulting composite. As noted above, the process is a foam-forming process that enables forming composites at high solids content (i.e.,

high consistency) without the need for the use of a forming wire and drainage. In the process, air content and foam density are characteristics of the foam in the process. Foam can be classified as either stable or unstable. However, overall, foams are relatively unstable thermodynamically. Foam stability depends on many factors including surfactant type and concentration, temperature, stabilizer concentration, and the presence of solids. Foam collapse occurs when liquid in foam moves to the bottom of the foam bubble by the force of gravity causing the lamellae on top of or between the bubbles to thin to the point of failure. See, Porter, M. R. Handbook of Surfactants, 2<sup>nd</sup> Ed., Blackie Academic & Professional (Chapman & Hall), 1994 pp 65-69. In the present process, the foam is considered to be stable.

To further understand the foam useful in the process, a discussion of foam air content and foam density is illustrative.

Wiggins-Teape teaches foams having an air content of at least 65% by volume (see, U.S. Patent Nos. 3,716,449 and 3,938,782). To effect dispersion, foams having an air content of 55-75% by volume (see U.S. Patent No. 3,871,952) or 50-70% by volume (see U.S. Patent No. 3,937,273). Outside this air content range (either higher or lower), solids in the foam, such as glassfiber, cellulose fiber, synthetic fiber, particulates, and the like, agglomerate. However, foam provides greater dispersion than a web or handsheet made from an aqueous slurry at the same solids content. Ahlstrom describes an improved process that uses an air content of 25-75% by volume (see U.S. Patent No. 5,904,809).

However, at high air contents (e.g., greater than about 75% by volume, Wiggins-Teape describes that the foam viscosity rises to the point where the liquid in the bubble lamellae can no longer be drained (within a reasonable time) from the mixture (e.g., the foam is a stable foam). Thus, forming on a foraminous support and draining the liquid from the web, like on a paper machine, is not practical. In the process of the invention, the high air content foam is a stable foam acts like a semi-solid and drainage of the liquid is slow. Because little liquid is available to drain out of the foam (for example, at 95% by volume air content, 1000 ml of foam contains only 50 ml of liquid), foam collapse by liquid movement (due to gravity or applied suction) takes a very long time. Total drainage time can be demonstrated as an exponentially decreasing rate as seen in FIGURE 1. In fact, complete liquid drainage

is never fully achieved. Consequently, this long drain time and the stiffness or high viscosity of the foam make conventional drainage impractical. The process of the invention makes use of high air content foam, typically greater than about 75% by volume. In one embodiment, the air content is greater than about 90% by volume, and in another embodiment, greater than about 98% by volume. Such high air content foams have not previously been practiced to produce a product that does not require a foraminous support through which free liquid is drained from the web. In the present process, foam collapse is initiated by temperature and/or by hygroscopic materials in the system that absorb liquid sufficient to effect foam bubble collapse.

Foam density is closely correlated with air content. In the references noted above, foam densities in the range of 250-500 g/l at 1 bar pressure are described. By eliminating the need for liquid drainage, lower foam densities can be used to form fibrous webs (for example, foam densities from about 20 to about 100 g/l yield air contents of from about 90 to about 98% by volume). In the present invention, foam densities between about 20 to about 200 g/l at 1 bar are useful. The elimination of the forming step in the process greatly reduces the equipment necessary. Because liquid is not drained from the foamed materials during web formation, there is no typical whitewater or reclaimed liquid or foam that needs to be reprocessed and reused. The reduced liquid/foam load also reduces the amount of liquid in the product leading to more economical drying. This is illustrated by examining the forming solids or consistency in the process.

The Ahlstrom patents describe a foam-forming process that uses a fiber consistency of up to 12% is possible in a foam having an air content of 25-75% by volume. The process of the invention makes use of fiber consistencies ranging from about 15 to about 50% by volume. In certain embodiments, fiber consistencies are between about 30 to about 50%. In other embodiments, fiber consistencies are between about 20 to about 35%. Dewatering of fiber at such high consistencies can be achieved. High solids fiber sludge can be further dewatered in an extruder with the addition of slip aids. Also, reclaimed fiber can be extruded at high consistencies with the slip aids in order to reclaim the fibers and fillers typically found in printing papers. In the present process, foam is used to fluidize the fiber as opposed to adding a slip aid. The foam is generated by the action of high speed screws in a counter or co-

rotating extruder or the high speed rotor of a rotary mixer/foamer or pump on a suitable surfactant. The foam used in the process includes a surfactant. A suitable surfactant is one which generates a foam density of about 100 g/l and an air content of about 90% with a surfactant concentration between about 0.01 to about 5 % by weight of the composite. In one embodiment, the surfactant is Incronam 30 produced by Croda.

High solids fiber are used in the process of the invention. High solids fiber can be produced from wet pulp that has been dewatered to greater than about 20% consistency or from dry fibers obtained via a hammermill and adding water. Thus, in the process of the invention, high solids compositions, with appropriate chemical additives including binders, latex, wet strength agents, dry strength agents, crosslinking agents, acids, bases, dyes, powders, pigments, polymers, can be mixed and foamed in a mixing device.

The process of the invention uses high consistency fiber that is fluidized with foam. An overall diagram of a representative method of the invention is illustrated in FIGURE 2.

The foaming and mixing operation can be achieved by a shear inducing mixing device. In one embodiment, the shear inducing mixing device a mixer/foamer, for example, Model 8M Mixer/Foamer available from E. T. Oakes Corporation, Hauppauge, NY. This device is a rotary mixer and is illustrated in FIGURES 3A-C. To fluidize the fiber, the fiber at roughly 30% solids is added to the device with a piston that pushes the fiber toward the rotor. At the shear or mixing point where the fiber contacts the rotor, surfactant is injected. The foamed fiber exits into a tube that feeds a die. Referring to FIGURES 3A-C, air and other chemicals can also be added along the radial axis of the rotor. Chemical additions can be made on the front face of the rotor or on the rear face. The rotor and stators are shown in the FIGURES 3B and C. In the device, the path that the fiber must take is tortuous and without adequate foaming the fiber plugs the rotor. A representative plate mixer extrusion device, method, representative products formed in accordance with the invention, and the performance characteristics of representative products are described in Example 2.

In another embodiment, the shear inducing mixing device is an extrusion device. One such extruder is the ZSK 58, a mega compounder available from

Coperion Corporation, Ramsey NJ. One possible configuration of the extruder is shown in FIGURE 4. In the process, pulp is added into the extruder at about 20 to about 40% solids. Then surfactant is added to initiate foaming. Additional chemicals

5 Crosslinking agent, (e.g., citric acid and catalyst) can be added and mixed with the fibers in the extruder making fibers that are prepared for crosslinking during subsequent drying of the product. Binders such as KYMENE (available from Hercules, Wilmington DE) and latex (available from DuPont, Midland MI or HB Fuller, St. Paul MN) can also be used. Chemicals and other binders in solid, liquid, or  
10 gaseous forms can be added. Air can also be added if needed to increase foaming and/or air content. A representative twin-screw extrusion device, method, representative products formed in accordance with the invention, and the performance characteristics of representative products are described in Example 1.

Using either device, (i.e., rotary mixer or twin-screw extruder), the foamed  
15 fiber and additives are extruded through a die to form a sheet or composite web. It is also possible to generate other shapes. The foam composite is extruded onto a solid conveyor belt, wire, or nonwoven carrier fabric to transport the web to the dryer. The foamed composite is then dried (and/or optionally cured) using techniques such as convection drying, through air drying, impingement, microwave, radio frequency, and  
20 the like.

The composites formed by the processes of the invention include acquisition and storage composites. The process of the invention enables the formation composites composed of any fiber, composites having low densities, and composites including in situ crosslinked fibers. For composites that include in situ crosslinked  
25 fibers, crosslinking agent can be added to the fibers before the fibers are added to the extruder. Alternatively, crosslinking agent can be added to the mixing device during the extrusion process.

To achieve suitable acquisition performance, acquisition composites have a relatively low density. The acquisition composite also has suitable absorption and  
30 desorption characteristics, referred to herein as the mid-point desorption pressure (MDP).

As shown in FIGURE 5, the density of composites produced by the process of the invention is much less than composites formed by the other noted processes. FIGURE 5 illustrates the difference between the present process and the process for two fiber furnishes. A pine only furnish can be produced typically at about  $0.14 \text{ g/cm}^3$  with a foam process for forming cellulosic composites described in PCT/US99/26560, Reticulated Absorbent Composite, and PCT/US99/05997, Methods For Forming A Fluted Composite. In a wetlaid system with traditional papermaking fibers, density can range from  $0.1\text{-}1.4 \text{ g/cm}^3$  depending on the grade (see Handbook of Pulp and Paper Technology by K. Britt, 1970, page 669). The present process can form a composite from the same fiber (pine) at a density of  $0.037 \text{ g/cm}^3$ . This density is less than the density at which foam laid, or high dilution wetlaid processes can form composites including crosslinked fiber.

Density is related to pore size distribution. The present process, by nature of both the agglomeration effects and the dispersion effects of foam, creates a web with a wide range of pore sizes. The pore sizes are measured by the autoporosimeter and confirmed by measurements taken from photomicrographs of the foam. The pore size distribution in the range less than  $750 \text{ um}$  can easily be measured by an autoporosimeter available from TRI/Princeton, Princeton, NJ. For a description of the theory, applications, and equipment, see Miller and Tyomkin in The Journal of Colloid and Interface Science (162, pages 163-170, 1994). The porosimeter tests a sample through an absorption and desorption cycle. Briefly, a presaturated sample is placed in the instrument. The pressure in the sample chamber is increased which causes the liquid in the sample to drain out from the largest pores first followed by the smaller pores. A computer interfaced with a balance monitors the amount of liquid leaving the sample at each pressure applied. After the last pressure point is tested, the system can run in reverse causing the sample to absorb liquid which is again tracked with pressure. From this data, pore size distributions and absorption/desorption hysteresis can be determined.

Mode pore size radius,  $\mu\text{m}$ , for similar webs made on several processes is shown in Table 1. Mode is defined as the pore size with the most volume which indicates the highest frequency of occurrence. These values indicate that the mode

pore sizes in composites formed by the present extrusion method (pore size contributing the greatest volume) are larger than those produced by other processes.

Table 1. Comparison of Mode Pore Size Radius ( $\mu\text{m}$ ).

Method	Extrusion	Foam	Airlaid	Wetlaid
Absorption Curve	330	225	210	250
Desorption Curve	150	88	98	75

5

The data in the above table are derived from the pore size distribution charts illustrated in FIGURES 6-9. FIGURES 6-9 illustrates the pore size distribution charts for representative composites formed by the present extrusion process, foam-formed, airlaid, and wetlaid processes, respectively. Each composite had a target basis weight of 300 g/m<sup>2</sup>. In these figures, mode pore sizes for absorption are indicated. Mode desorption pore sizes are not marked, but can be determined as for the absorption.

Low values for capillary desorption pressure (CDP) have been indicated as being preferred acquisition composites. Capillary desorption pressure (CDP) is defined as the head pressure at which 50% of the liquid in a saturated sample has been drained from the sample. For fluid acquisition, a value of capillary desorption pressure of 8-40 cm H<sub>2</sub>O (8-25 cm H<sub>2</sub>O typical) is advantageous for a synthetic foam to acquire fluid (see, e.g., U.S. Patent No. 5,571,849; U.S. Patent No. 5,550,167; U.S. Patent No. 5,851,648). For fluid distribution, values of 12-50 cm H<sub>2</sub>O (20-40 cm H<sub>2</sub>O typical) for CDP are desired for good performance (see U.S. Patent No. 6,013,589).

As noted above, Miller and Tyomkin show that the capillary desorption pressure can be determined from a plot of percent saturation vs. applied pressure obtained from the autoporosimeter. Absorption (uptake) and desorption (retention) curves over a range of pressure give an indication of a material's ability to acquire and retain liquid. Acquisition materials for use in absorbent products such as infant diapers must be able to quickly absorb liquid and also efficiently release it again to the diaper core. The capillary desorption pressure measured by the autoporosimeter is called the mid-point desorption pressure (MDP). The MDP can be used as a measure of a material's ability to function as an acquisition material. It is clear that any percentage of saturation could be chosen and, for simplicity, the mid-point of the curve

has been chosen as it is close to the inflection point of the curve. Other than the materials formed by the present process, no cellulose materials have to this point in time been unable to achieve MDP values less than 14 cm H<sub>2</sub>O. Thus, cellulose-containing materials that exhibit lower MDP values result in improved acquisition performance.

In one embodiment, the composites of the invention have an MDP value less than about 14 cm H<sub>2</sub>O. In another embodiment, the composites have an MDP value less than about 12 cm H<sub>2</sub>O. In a further embodiment, the composites have an MDP value less than about 10 cm H<sub>2</sub>O.

To illustrate the current performance of cellulose-based acquisition materials, consider an airlaid acquisition material composed of southern pine fibers. Using the TRI autoporosimeter, the MDP was determined to be 44 cm H<sub>2</sub>O. This data is presented in FIGURE 10 to show the output of the autoporosimeter.

The use of crosslinked cellulosic fibers in personal care absorbent products such as infant diapers has improved the performance of current diapers in the market. Several airlaid pads were made from two crosslinked fibers were tested for MDP. A pad made from citric acid crosslinked fibers (Chemistry B) had an MDP of 24.2 cm H<sub>2</sub>O. A pad made from polyacrylic acid/citric acid crosslinked fibers (Chemistry A) had an MDP of 14.4-15.9 cm H<sub>2</sub>O. Chemistry C refers to polyacrylic acid crosslinked fibers

The process of the invention provides webs having improved MDP values. For example, an extruded pine fiber web formed by the Oakes mixer/foamer without using a crosslinking chemistry provides an MDP value of 18.5 cm H<sub>2</sub>O (compare to 44 cm H<sub>2</sub>O for airlaid). The MDP value of an extruded web formed from fibers crosslinked with a blend of polyacrylic and citric acids (pre-crosslinked Chemistry A) was measured to be 10.5 cm H<sub>2</sub>O (compare to 15.2 cm H<sub>2</sub>O for airlaid). The MDP value of an extruded web formed from citric acid crosslinked fibers (pre-crosslinked Chemistry B) was measured to be 12.0 cm H<sub>2</sub>O (compare to 24.2 cm H<sub>2</sub>O for airlaid).

The extrusion process provides MDP improvement due to the web's structure and surface tension effects. Surface tension relates to pressure difference as shown in the Laplace equation:

$$r = \frac{2\sigma}{\Delta P} \cos \theta$$

where  $\Delta P$  = pressure difference,  $\sigma$  = surface tension,  $\theta$  = contact angle, and  $r$  = radius.

If the surface tension is reduced due to the presence of surfactants (as in the foam extrusion process of the invention), then at constant radius, the pressure difference (in effect the MDP) must also be reduced. But most pores collapse when wet unless there is resistance to collapse. Further improvements can be gained by increasing the bonding in the structure through interfiber crosslinking and/or the addition of binders. If bonding and fiber resilience increases, then the pore radius will not collapse yielding again lower MDP values (by minimizing the rise in pressure due to collapsing pore radius). The addition of latex raises the value of the contact angle and thus lowers the cosine. This also at constant pore radius demands a reduction in MDP.

The improvements described above are graphically represented in FIGURES 11 and 12. FIGURE 11 is a bar graph that demonstrates the reduction in mid-point desorption pressure as a function of crosslinking chemistry for the present process. Extruded composites formed from pine fibers, citric acid crosslinked fibers, and in situ citric acid crosslinked fibers (i.e., fibers added to mixing device that were treated, but not cured, with citric acid) had MDP values of 18.5, 12.0, and 9.8 cm H<sub>2</sub>O, respectively. FIGURE 12 is a graph that shows the effect of increasing crosslinking agent on MDP for extruded composites including fibers crosslinked with a blend of polyacrylic and citric acids (pre-crosslinked Chemistry A), citric acid crosslinked fibers (pre-crosslinked Chemistry B), in situ citric acid crosslinked fibers (in situ Chemistry B), and in situ polyacrylic acid crosslinked fibers (in situ Chemistry C). As the amount of crosslinking agent is increased, the MDP value for composites made from these fibers decreases. A reduction in MDP (from 12 to 9.8 cm H<sub>2</sub>O) is shown by the dotted lines compared to the solid pre-crosslinked Chemistry B line. Chemistry C shows an even greater reduction in MDP.

The addition of latex, such as PD8161 from HB Fuller, St. Paul MN, (e.g., 5% by weight based on total weight of composite) also positively impacts the MDP and improves the acquisition performance. FIGURE 13 illustrates that latex alone and latex combined with in situ crosslinking reduce MDP. Again, the pre-crosslinked data

is considered the control to show the effects of in situ crosslinking (previously demonstrated as from 12 to 9.8 cm H<sub>2</sub>O). The effect of latex without in situ crosslinking is a drop in MDP from 12 to 9.5 cm H<sub>2</sub>O. The combined effect of in situ crosslinking and latex addition changes the MDP from 9.8 to 8.3 cm H<sub>2</sub>O. At higher levels of latex, even lower MDP values are obtained. As an example, the MDP of a pre-crosslinked Chemistry A fiber composite with 15% latex was 7.7 cm H<sub>2</sub>O. A summary of the MDP values is provided in Table 2.

Table 2. MDP Values for Representative Extruded Composites.

Fiber Type	Chemistry Level %	MDP Values, cm H <sub>2</sub> O		
		Airlaid Sample	Extruded without latex	Extruded with latex
Southern pine	0	43.4-44.5	16.2-18.5 (E & O)	4.8-10.7 (E & O)
Pre-crosslinked		14.4-24.9	11.5-12.1	4.7-9.1
Chemistry A	13	14.4-15.9	10.5 (O)	7.7-9.1 (O)
Chemistry B	6	23.8-24.9	12.0 (O)	4.7-9.0 (E & O)
Chemistry C	6	-	11.5 (O)	-
Crosslinked in situ			9.1-13.5	7.6-8.8
Chemistry A	-	-	-	-
Chemistry B	2-6	-	9.8-13.5 (O)	7.5-8.8 (O)
Chemistry C	2-6	-	9.1-11.0 (O)	7.6-8.3 (O)
Blend 50% pine/50% pre-crosslinked Chemistry A	13*	-	12.6 (O)	8.1-10.4 (O)

10

\*only applies to fiber that is cross linked

(E) = samples made on twin screw extruder

(O) = samples made on Oakes Mixer/foamer

(E&O) = includes samples made on either Oakes Mixer/foamer or twin screw extruder

The acquisition rate of extruded composites formed in accordance with the present invention was determined. Acquisition rate was determined as described in U.S. Patent No. 5,460,622 and U.S. Patent No. 4,486,167, each of which is incorporated herein by reference. The only change to the procedure was that 75 ml gushes were used so that the total loading was closer to the total capacity of the diaper making the test more stringent.

Commercial diapers were purchased (PAMPERS by Procter & Gamble) and tested for 4<sup>th</sup> gush acquisition rate by the indicated procedures. The commercial diapers exhibited an acquisition rate of 0.44 ml/sec for the 4<sup>th</sup> gush of 75ml. This performance represents the current state of the art. In situ crosslinked acquisition patches were produced with both Chemistry B (citric acid crosslinked fibers) and C (polyacrylic acid crosslinked fibers) at levels of 4 and 6%. These patches were then inserted into a commercial diaper (PAMPERS of the same size and type as the control). The insertion was accomplished in the following manner. The cover stock was carefully cut at one end of the diaper and peeled back to expose the commercial acquisition patch and carrier tissue. These materials were carefully removed without disturbing the diaper core. The representative extruded patch of the same dimensions as the commercial patch was inserted into the diaper. The cover stock was returned to its original position and sealed.

At the 4% crosslinking agent level, 4<sup>th</sup> gush acquisition rates ranged from 0.48-1.13 ml/s depending on chemistry type. As a second control, pre-crosslinked fibers were also tested. At the 6% level, the rate ranged from 0.36-1.60 ml/s depending on basis weight and chemistry type. These data demonstrate marked improvement in acquisition rate for extruded composites versus a commercial diaper control and versus acquisition materials produced from pre-crosslinked fibers. This improvement is especially important as the crotch area of diapers decreases thus reducing the area available to acquisition. The acquisition data is summarized in Table 3.

Table 3. Acquisition Rates for Representative Extruded Composites.

Sample Number	Basis Weight g/m <sup>2</sup>	In situ Chemistry	In situ Level %	Latex Level %	4 <sup>th</sup> Gush Acquisition Rate ml/s
45-1	300	B	6	5	0.88
45-2	200	B	6	5	0.87
45-3	300	B	6	0	0.49
45-4	200	B	6	0	0.36
45-9	300	C	6	5	1.60
45-10	200	C	6	5	1.05
45-11	300	C	6	0	0.77
45-12	200	C	6	0	0.58
45-17	250	C	4	2.5	1.09
45-18	250	C	4	2.5	1.01
45-19	250	C	4	2.5	1.13
45-20	250	C	4	2.5	1.07
45-21	250	B	4	2.5	0.68
45-22	250	B	4	2.5	0.51
45-23	250	B	4	2.5	0.48
45-24	250	B	4	2.5	0.62

5 The extruded composites of the invention also exhibit advantageous tensile strength. Tensile was determined by a horizontal tensile method because many of the samples tested are very weak (e.g., air laid fluff pads). The method uses a horizontal jig fixed to the lower cross head of a constant rate extension tensile machine like those provided by Instron. A 10cm x 10cm sample is clamped into the jig. The load cell is re-zeroed for each sample. The sample is then pulled by the tensile machine. The machine measures the elongation and failure load for each sample.

10 In situ crosslinked samples were produced with two different chemistries and at three levels. Tensile data from these samples are shown in the table and chart below.

It is clear that as in situ chemistry levels increase, the tensile increases. This increase is an indication of an increase in interfiber bonding. All samples (except those indicated as pre-crosslinked) were produced in the same manner with only the variation in chemistry type and level as indicated in Table 4.

Table 4. Tensile Strength for Representative Extruded Composites.

Chemistry Level and Type	Basis Weight g/m <sup>2</sup>	Tensile g/in	Tensile std dev
0% Chemistry B	287	31	24
2% Chemistry B	304	24	2.7
6% Chemistry B	313	58	6.8
Pre-Crosslinked with 6% Chemistry B	288	5.0	0.4
0% Chemistry C	287	31	24
2% Chemistry C	293	78	17
6% Chemistry C	294	97	33
Pre-Crosslinked with 6% Chemistry C	323	4.5	0.6

Level based on fiber weight; all samples extruded using Oakes mixer/foamer.

Depending on the cross linking chemistry applied, the tensile rose 10-20X when in situ crosslinking was employed. FIGURE 14 illustrates the effect on in situ crosslinking on extruded composite tensile strength.

Latex can be used to increase the strength of extruded composite structures and webs. The effect of latex and fiber blend on the strength of representative extruded composites is illustrated in FIGURE 15. The effect of latex and crosslinking chemistry on the strength of representative extruded composites is illustrated in FIGURE 16. Referring to FIGURES 15 and 16, the strength of a Chemistry B sample is 34 g/in with 6% chemistry (BW = 205 gsm). The pre-cross linked Chemistry B composites with 5 % latex is 94 g/in (BW = 157 gsm). A composite with 5% latex and 6% in situ cross linking has a tensile of 1065 g/in (208 gsm), which is more than ten times greater than either treatment alone.

In a further aspect, the present invention provides absorbent articles that include the crosslinked cellulosic fibrous product. The product can be combined with one or more other layers to provide structures that can be incorporated into absorbent articles such as infant diapers, adult incontinence products, and feminine care products.

## EXAMPLES

### Example 1

#### Representative Twin-Screw Extrusion Device and Method, and Representative Products and Their Performance Characteristics

In this example, a representative twin-screw extrusion device, method for forming the product using the device, representative products formed by the method using the device, and the performance characteristics of the representative products are described.

Laboratory tests demonstrated that extruding a fibrous web in a foam media provides enhanced performance possibilities. In view of the laboratory successes, pilot trials were conducted. The following describes the use of twin screw extruders produced by Krupp, Werner, and Pfleiderer (KW&P) in the process of the invention to provide representative products of the invention.

In the trial, a continuous web of material was extruded with a wide range of basis weight ( $\sim 400\text{-}2000\text{ g/m}^2$ ). A bicomponent fiber (CELBOND T105) was fed into the system to produce samples with more integrity. The surfactant concentration was tested at two levels: 1% and 0.5% of the total mass. Both levels produced adequate foam. Foam quality was similar to that from the Oakes lab unit (plate mixer/foamer; 94-99% air content; foam density 10-60 g/l). The opening of the fibers did not damage the fibers with respect to fiber length. Product quality and performance was not optimized and is therefore not as satisfactory as the samples prepared with the Oakes system. The extruder units are compact and, depending on the screw diameters, can be installed on a concrete slab without footings or pilings. The small size and simplicity of the process also translates into low capital and engineering costs compared to typical paper industry. The ability to add SAP directly to the equipment in dry form is an advantage.

Equipment. A nine barrel ZSK 58mm twin screw extruder (KW&P) was used for the trials. A diagram of the extruder set up is given in FIGURE 4. Four Acrison single screw feeders were used to feed the raw materials to the extruder. A total of five different screw designs were used to disperse the fibers and generate foam. The different screw designs are described in the following section.

The device shown in FIGURE 4 shows several features worth noting. The first is the relative size of the equipment. The extruder was contained within an area approximately 25' x25'. The extruder was on the main floor while the feeders were on the second floor. Each barrel is less than 1 foot long. In a commercial design for absorbent products, a nine barrel system is not needed (note: counting from the left, the first and last barrels are not necessary). The third barrel may also be optional.

Another important point is simplicity. This system is basically a mass in, mass out operation. The feed systems are simple, employing known technology: loss weight feeders. This point is underscored when absorbent material (e.g., superabsorbent polymer, SAP) can be added in a dry form via a side feeder directly into the wet fiber flow without plugging. This system was easily able to process the fiber and the SAP which met the first two trial objectives. Addition of SAP at the very end of the process in a dry form kept SAP swelling to a minimum with SR1001 (a lightly crosslinked polyacrylate available from Stockhausen). Another polyacrylate from Stockhausen, SXM-77, swells and negatively affects runnability when fed dry with a retention time in the extruder of under 5 seconds.

Experimental Details. Extruder trials were conducted with a series of runs. These runs are outlined in Table 7. Without fiber, foaming was no problem and the foam generated was in the 96-97% air content range (compare to a theoretical optimum 67% for a foam-forming process (foam laid) described in PCT/US99/26560, Reticulated Absorbent Composite, and PCT/US99/05997, Methods For Forming A Fluted Composite, each expressly incorporated herein by reference in its entirety). Foam density was 29-30 g/l compared to typically 350 g/l for the foam laid processes. After achieving foam, the fiber feed was started. To obtain fiber dispersion, three different screw configurations were tried. The first configuration had quite a few high shear elements. While these elements generated shear, they also restricted the flow of material (e.g. increased retention time). This design generated some heat and was not efficiently dispersing the fibers. The second design was a low shear design with no restrictions. This design enabled a 1000 rpm screw speed without significantly increasing the temperature. As a result, the fiber dispersion improved. Fibrous knots were still visible in the web. However, the dispersion was better than the first screw

design and better than the dispersion achieved in this trial, identified below as 1051-XNP.

The third design reinserted a limited number of higher shear elements to improve the fiberization. These few shear elements increased the temperature.

5        The fourth screw design (similar to the second design but with more kneading blocks) allowed feed up to 225 lb. OD fiber/hr (2.5 ton/day). Processing fiber only, this screw design appeared to break up the fiber chunks. Feed was reduced to 0.5 ton/day so that the fiber dispersion could be more easily seen. The slot die was then installed which produced a web of approximately 500 g/m<sup>2</sup> and 0.05 g/cc (26.6%  
10    "couch" solids).

After taking samples and machine data, SR1001 was added at about the 50% level. The side feeder worked perfectly with no SAP feed issues. This composite (BW ~1100 g/m<sup>2</sup>, density ~0.11g/cc) was extruded through the die head and samples were taken (39% "couch" solids). Capacity values were 16 g/g. When SXM-77 was  
15    tried, all the free moisture was removed and dry chunks of SAP and fiber were generated. This is the same result seen in a previous trial (1050-XNP).

Since webs could be produced with the die, samples were produced with SAP at lower basis weights to compare to foam laid materials previously made and tested. Bicomponent fiber CELBOND T105 was also added to increase integrity. Wet  
20    strength agent KYMENE, an alternative to the bicomponent fiber can also be added into the system. Low basis weight materials were produced. Surfactant level was reduced to 0.5% of the total mass from 1% with no detrimental effects. Empirically, water availability is more the limiting factor than the gross amount of surfactant.

Additional low basis weight materials with and without CELBOND T105 were  
25    formed with a fifth screw design using some three lobe elements. The material appeared to have fewer knots. Throughput studies were conducted which determined that this screw limited the fiber feed to 700 lb./hr (as is) or about 1170 lb./hour total mass (assuming 40% solids and 50% SAP).

Fiber Quality/Dispersion Results: Screw Design and Throughput. Samples of  
30    material from several screw shaft designs were tested for percent knots and fiber length. These two tests are typically used by the fluff lab to evaluate hammermill efficiency. These tools were used to evaluate the different screw designs. Table 5

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indicates that Design 5 appears to be slightly better than Design 4 based on the sonic fractionation data. In either design, the fibers are not being cut as evidenced by the fiber length data.

Table 5. Comparison of Fiber Quality for Screw Design 4 and 5.

Sample	Screw Design	Knots %	FQA LWAFL mm	Fines %	Curl Index	Kink Angle
Fiber Only, Run 19A	4	-	2.47	5.0	0.19	1.9
Run 19 with SAP	4	22.7	2.54	6.0	0.16	1.7
Run 31A	5	10	2.47	4.6	0.15	1.7

Other data indicated that Design 2 was least effective while the subsequent designs improved the fiber dispersion.

Solids Content. Percent solids were measured in the 25-65% range, but do not follow predicted values based on material balances (17-47% range). All measured values except one indicate higher solids than the theoretical values which indicates that the samples may not have been completely dry.

Capacity Results. Capacity under load values of about 11-17g/g were measured on samples containing SAP contents of 37-46%. Capacity values were reasonable considering the high basis weights and the increasing density due to a constant die slot size.

Surfactant Level. Three levels of surfactant (Incronam 30 available from Croda) were used 5.0, 7.5 and 10.0 (as is) lb./hr. Surface tension values from water extracts indicate that the surfactant was present on the surface and easily removed. The surface tension values were 40.7, 40.4, and 35.5 dyne/cm for the three surfactant levels (5.0, 7.5 and 10.0 lb./hr). As foaming was successful at all levels and there is no "wash" step in this process, lower levels of surfactant can be utilized to reduce the level of residual surfactant. Lower levels of surfactant can enhance the product's acquisition performance. Typical extract surface tension values in foam laid webs using Incronam 30 or Dehyton K were 40-43 dyne/cm.

Acquisition/Pore Size Distribution/Median Desorption Pressure. Acquisition was measured by the Edana test method, the new Market Pulp Standard. Acquisition

times for a Procter & Gamble PAMPERS control is 27 seconds, 60 seconds, and 85 seconds for the first through third doses of 100 mL, respectively. Acquisition performance of the representative samples indicated the presence of excess surfactant. The first dose acquisition time was between 30 and 70 second for all samples. In  
5 general, the second and third doses took longer than 300 seconds (5 minutes).

Pore size distribution and median desorption pressure for representative products are presented in the Figures.

The pore size distribution (PSD) and the median desorption pressure (MDP) do not provide additional insight beyond the surfactant level as to the acquisition  
10 performance. FIGURES 17-20 above show the PSD and MDP for two lower basis weight samples produced during this trial. When compared to FIGURES 21 and 22, the 1051-XNP samples are very similar to those produced on the Oakes during laboratory study described in Example 2. MDP data does not show any differences either between the two studies. The MDP values for runs 17 and 19 were measured to  
15 be 17.2 cm H<sub>2</sub>O and 16.2 cm H<sub>2</sub>O, respectively, while the value for 100% pine in the Oakes process was 16.5 cm H<sub>2</sub>O.

Comparison to Similar Foam Laid Materials. Table 6 below shows a comparison of materials in accordance with the invention versus foam laid made materials. Notable differences are the density and the resulting effect on vertical  
20 wicking. Capacity values are similar despite differences in wood fluff pulp (southern pine) content. Even without optimization, the 1051-XNP material is comparable to the foam laid made materials.

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Table 6. Comparison of 1051-XNP and Foam Laid (943 and 946) Samples.

Test\Sample	943-XNP	1051-XNP- 31A	946-XNP
Basis Weight, g/m <sup>2</sup>	420	425	411
Density, g/cm <sup>3</sup>	0.13	0.09	0.14
SAP Content, % total mass	20	37	35
SAP Type	SR1001	SR1001	SR1001
Pine Content, % of fiber	60	100	50
Capacity under Load, g/g	13	16	17.5
Vertical Wicking, cm @ 15 min	-	5	10.5

Throughput. Throughput studies indicate that ~450 OD lb./hour (5 ton/day) of  
5 total mass can be processed through the 58 mm machine.

Table 7. Summary of Representative Extruded Composites.

Sample	1	2	3	4	5	6	7
Screw Number	1	2	2	2	2	2	2
ZSK RPM	400	400	400	600	600	600	1000
ZSK Torque (%)	40	11	14	6	7		5
Total Rate (as is lb./hr)	450	450	530	530	570	590	610
Product Temperature (°C)	89	47	53	40	38	-	29
T1	25	25	25	25	25	25	25
T2	28	27	29	28	28	28	27
T3	33	26	28	28	29	29	29
T4	69	32	36	33	32	31	30
T5	101	38	45	38	35	34	32
T6	86	31	43	42	39	36	35
T7	87	40	49	39	37	34	30
T8	67	30	40	36	33	31	29
Fiber (as is lb./hr)	400	400	480	480	480	480	480
SAP (as is lb./hr)							
Water (as is lb./hr)	40	40	40	40	80	100	120
Surfactant	10	10	10	10	10	10	10
Air							
CELBOND T105							

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Sample	8	9	10	11	12	13	14
Screw Number	3	4	4	4	4	4	4
ZSK RPM	1000	1000	1200	1200	1200	1200	1200
ZSK Torque (%)	8	5	5	6	6		5
Total Rate (as is lb./hr)	600	620	620	870	1070	620	420
Product Temperature (°C)	54	29	29	30	38		
T2	27	26			27		
T3	30	25			27		
T4	32	29			30		
T5	42	29			31		
T6	45	27			29		
T7	39	26			29		
T8	39	27			35		
Fiber (as is lb./hr)	470	500	500	750	750	300	300
Water (as is lb./hr)	120	110	110	110	110	110	110
Surfactant	10	10	10	10	10	10	10
SAP (as is lb./hr)					200 SXM	200 SXM	
Air					yes	yes	
CELBOND T105							

1000244-14001

Sample	15	16	17	18	19	19A	20
Screw Number	4	4	4	4	4	4	4
ZSK RPM	1200	1200	1200	1200	1200	1200	1200
ZSK Torque (%)	4	4	4	4	3	3	3
Total Rate (as is lb./hr)	270	190	270	315	158	135	158
Product Temperature (°C)	26		25		27	27	31
T2	24		25				27
T3	26		26				28
T4	26		26		29	29	29
T5	26		26		29	29	29
T6	28		26		29	29	30
T7	24		25		29	29	30
T8	27		26		29	29	29
Fiber (as is lb./hr)	150	150	150	150	75	75	75
Water (as is lb./hr)	110	30	110	110	55	55	55
Surfactant	10	10	10	10	5	5	5
SAP (as is lb./hr)				45-SR	23	0	23
Air	yes	yes	yes	yes	yes	yes	yes
CELBOND T105							yes

T04T05T06T07T08T09T10T11T12T13T14T15T16T17T18T19T20T21T22T23T24T25T26T27T28T29T30T31T32T33T34T35T36T37T38T39T40T41T42T43T44T45T46T47T48T49T50T51T52T53T54T55T56T57T58T59T60T61T62T63T64T65T66T67T68T69T70T71T72T73T74T75T76T77T78T79T80T81T82T83T84T85T86T87T88T89T90T91T92T93T94T95T96T97T98T99T100

Sample	21	22	23	24	25	26	27	28
Screw Number	4	4	4	4	4	4	4	4
ZSK RPM	1200	1200	1200	1200	1200	1200	1200	1200
ZSK Torque (%)		3		4	4		4	4
Total Rate (as is lb./hr)	310	313	414	619	719	819	919	1170
Product Temperature (°C)		29		28	29			31
T2				27	27			29
T3				28	28			30
T4				29	29			31
T5				29	29			32
T6				29	30			32
T7				29	29			31
T8				30	31			33
Fiber (as is lb./hr)	150	150	200	300	400	500	600	700
SAP (as is lb./hr)	45 SR	45-SR	60-SR	90-SR	90-SR	90-SR	90-SR	210-SR
Water (as is lb./hr)	110	110	146	219	219	219	219	250
Surfactant	5	7.5	7.5	10	10	10	10	10
Air	yes	yes	yes	yes	yes	yes	yes	yes
CELBOND T105								

100044-4401

Sample	29	30	31	31A	32	33	34
Screw Number	4	5	5	5	5	5	5
ZSK RPM	1200	1200	1200	1200	1200	1200	1200
ZSK Torque (%)	5	7	3	3	3	4	
Total Rate (as is lb./hr)	1170	1260	158	158	310	620	1220
Product Temperature (°C)	33	42	26	30	30	30	
T2	28	30	28	28	28	28	
T3	29	30	29	29	29	29	
T4	31	33	30	30	30	29	
T5	32	37	32	32	32	30	
T6	31	33	31	31	31	30	
T7	31	37	29	29	29	30	
T8	34	41	31	31	31	31	
Fiber (as is lb./hr)	700	1000	75	75	150	300	700
SAP (as is lb./hr)	210- SR		23 SR	23 SR	45 SR	90	210
Water (as is lb./hr)	250	250	55	55	110	220	300
Surfactant	10	10	5	5	5	10	10
Air	yes	yes	yes	yes	yes	yes	yes
CELBOND T105							

T002944-11401

Example 2Representative Plate Mixer Extrusion Device and Method, and Representative Products and Their Performance Characteristics

5 In this example, a representative plate mixer extrusion device, method for forming the product using the device, representative products formed by the method using the device, and the performance characteristics of the representative products are described.

10 A plate mixer/extrusion process is one alternative to traditional forming techniques used to make composite core materials. In this example, the Oakes Mixer/Foamer (Oakes Continuous Mixing Head, E.T. Oakes Corporation, Hauppauge, NY) was used to generate an extrudable foam from which webs were made by extrusion through a simple die head. Three fiber furnishes were used: southern pine pulp fibers (CPine); citric acid-treated cellulosic fibers (XLA); and a 50:50 blend of these two fibers. PD8161 latex from H. B. Fuller Company was used as the binding and resiliency aid in levels of 5, 10, and 15% by weight.

As used herein, the term "EXPRO" refers to the extrusion process of the invention and the products formed by the process.

20 The results demonstrate the following. The device and method can form pine and treated fibers into webs at densities lower than other current processes. The average pore size radii for these products are larger for extruded webs than webs formed by traditional processes. The products have improved acquisition over current materials. The products exhibit much lower median desorption pressure values than current materials formed with traditional processes. The extrusion process has minimal waste of raw materials or product

25 General. In this example, CPine, XLA, and PD8161 latex were used to form samples with different fiber furnishes and latex contents. The sample descriptions are shown in Table 8.

Table 8. Extruded Composite Sample Descriptions.

Sample	Fiber	Latex Addition
1	100% Pine	0%
2	100% Pine	5%
3	100% Pine	10%
4	100% Pine	15%
5	100% XLA	0%
6	100% XLA	5%
7	100% XLA	10%
8	100% XLA	15%
9	50:50 Pine: XLA	0%
10	50:50 Pine: XLA	5%
11	50:50 Pine: XLA	10%
12	50:50 Pine: XLA	15%

Oakes Setup. To produce these samples, a laboratory apparatus was used as shown in FIGURES 3A-C. The specific machine and run specifications are given below.

In general, the desired pulp fiber, along with 2% by weight Polyox (4 million molecular weight polyethylene oxide) as a slip aid, was fed into the mixer/foamer via a piston feeder at 30% consistency. Other additives such as air, surfactant and latex were added via piston feeders to injection ports located on the Oakes device. The current system was a batch operation which operates on a mass in, mass out basis with essentially no waste. The target basis weight of the samples ( $300 \text{ g/m}^2$ ) was controlled by the pulp feed rate and the conveyor speed.

Pore Size Distribution. Pore size distribution is measured with the TRI autoporosimeter. Several examples are discussed here. The three samples chosen here represent the differences seen among three furnishes: pine (sample2, FIGURE 23), XLA (sample 6, FIGURE 24), and the 50:50 blend (sample 10, FIGURE 25).

In FIGURE 24, note the shift in the curves to higher average radii of each curve. This is indicative of the change from pine to crosslinked fiber. FIGURE 25,

the blend sample, shows an intermediate mode value between those seen in FIGURES 23 and 24. The larger average radius is a result of the stiffer crosslinked fibers forming a less dense web and also due to support by the structure. The area under the curve is indicative of the total volume in the sample and thus the capacity of the sample. This arises from the fact that the PSD curves are the derivative of the cumulative volume chart obtained from the autoporosimeter. Thus fiber furnishes can be evaluated based on their impact on pore size which in turn impacts the volume or capacity of the structure.

However, it is best to compare processes based on only the mode pore size with respect to acquisition. These values are listed in Table 1. These data indicate that the extrusion process of the invention generates the largest pore sizes of the four processes tested.

Acquisition. Acquisition performance is typically based on the results of a multiple dose test. The fourth gush results, being the most stringent conditions, are often used as an indicator of performance. The fourth gush results for the samples in this study are shown in the summary data table in Table 9.

In general, the XLA results were the most promising. These results are given in FIGURE 26. These data show that the acquisition rate improves with XLA alone over the current diaper controls. When latex is present, the results continue to improve over the control and over the performance of 1012-XNP. The fourth gush results are not the only improvement. All gushes (1-4) show improved acquisition rate versus the control.

Median Desorption Pressure. While it is important for an acquisition material to acquire fluid quickly, the material also must be able to readily release it to the absorbent core. This ability to release fluid is judged by the median desorption pressure. This is the pressure where 50% of the acquired fluid has been removed from the sample during testing on the autoporosimeter.

Composites formed from citric acid crosslinked fibers have an MDP of approximately 20-22 cm H<sub>2</sub>O. Composites formed from fibers such as XLA have only been able to achieve MDP values of 16-19 cm H<sub>2</sub>O. FIGURE 29 shows an example where XLA was used to produce the samples in 1012-XNP. Here the MDP was 17 cm H<sub>2</sub>O.

Using the extrusion process, MDP values for composites formed from citric acid crosslinked fibers alone were reduced to 10.5 cm H<sub>2</sub>O (see FIGURE 28). Addition of latex improved the MDP to 7.7 cm H<sub>2</sub>O (see FIGURE 27). Based on the range of MDP with fiber furnish shown in Table 9, it appears possible to control an MDP between 8 and 17 cm H<sub>2</sub>O using these fibers, latex, and the extrusion process.

These results show that different processes form different structures in terms of density and pore size distribution. These structural differences, along with surface characteristics, also impact the median desorption pressure.

FIGURES 29, 30, and 31 show the MDP of composites formed by three different processes. FIGURE 31 shows airlaid pads made from two batches of XLA fiber: identified as 46-01 and 46-02. These pads have a density of 0.06 g/cm<sup>3</sup> but do not have any surface active agents to inhibit the MDP (14-16 cm H<sub>2</sub>O). FIGURE 29 as noted previously is a foam-formed composite. Despite the lower density, the MDP is slightly higher than the airlaid samples. FIGURE 30 shows the MDP for a wetlaid composite. This material has an MDP of 18.5 and a similar density to the foam-formed sample. As seen in FIGURES 27 and 28, samples formed by the extrusion process exhibit much lower MDP values.

Tensile. Changes in tensile follow expected trends: (1) as the pine content increases, tensile increases; (2) as the crosslinked fiber content increases, tensile decreases; and (3) as the latex content increases, tensile increases. These samples were measured with an Instron using a horizontal jig.

The result can be summarized as follows. The density of the extruded webs is lower than other processes of forming absorbent webs, when pine or crosslinked fibers are used. Average pore size radii are larger for extruded webs providing enhanced acquisition performance. The extrusion process is capable of producing webs with improved MDP using pine and crosslinked fibers which indicates this material will release liquid into a storage core more easily. The extrusion process is capable of adding latex and other additives to a web without spraying and without waste.

The effect of latex and fiber blend on extruded composite strength is shown in FIGURE 15.

Table 9. Representative Extended Composite Performance.

Sample	Average Run Basis Weight <sup>b</sup> g/m <sup>2</sup>	Average Run Density g/cm <sup>3</sup>	MDP cm H <sub>2</sub> O	MAP cm H <sub>2</sub> O	MUP g/g	4 <sup>th</sup> Gush Acquisition <sup>a</sup> ml/s	Horizontal Tensile g/in
1	287	0.0372	16.5	8.6	7.6	0.16	31
2	323	0.0374	11.2	6.1	10.9	0.26	423
3	308	0.0363	10.8	6.0	10.5	0.29	1503
4	315	0.0379	11.3	6.2	9.9	0.35	2329
5	249	0.0387	10.5	4.5	12.1	0.61	15
6	305	0.0273	9.1	4.1	16.7	1.13	54
7	346	0.0287	8.7	3.8	17.2	0.91	123
8	326	0.0284	7.7	3.8	16.0	1.49	269
9	280	0.0306	12.6	6.3	11.3	0.28	24
10	285	0.0281	10.4	5.2	12.8	0.46	447
11	284	0.0286	8.2	4.1	14.7	0.83	806
12	316	0.0281	8.1	4.1	14.7	0.54	888
1012-XNP	285	0.044	17.0	5.9	13.8	0.92	1200
Airlaid 46-1 <sup>c</sup>	289	0.0646	14.4	5.5	15.0		
Airlaid 46-2 <sup>d</sup>	316	0.0663	15.9	6.1	14.2		
Wet Laid TR867	319	0.0430	18.5	5.0	14.4		
Control Diaper						0.44	

<sup>a</sup>Samples were tested in current Procter & Gamble PAMPERS surrounds with an airlaid/SAP core. The same commercial diaper was used as the control.

5 <sup>b</sup>Samples closest to 300 g/m<sup>2</sup> were chosen for testing. Average basis weight indicates how close the process settings (fiber feed and conveyor speed) were to achieve the target basis weight.

<sup>c</sup>XLA fiber (WTC)

<sup>d</sup>XLA fiber (CMF)

Example 3Performance Characteristics of Representative Products

In this example, the performance characteristics of representative products formed in accordance with the invention are described.

5       The medium uptake pressure (MUP), medium desorption pressure (MDP), and caliper of representative products of the invention were determined and compared to conventional airlaid webs. The normalized results are presented in Table 10. In Table 10, XLA refers to an airlaid web of cellulosic fibers crosslinked with citric acid; XLB refers to an airlaid web of cellulosic fibers crosslinked with a combination of citric and polyacrylic acid fibers; EXPRO-D refers to a composite of cellulosic fibers crosslinked with citric acid; EXPRO-E refers to a product of the invention formed from cellulosic fibers treated with citric acid; and EXPRO-F refers to a product of the invention formed from cellulosic fibers treated with a combination of citric and polyacrylic acid and latex. All samples tested at 300 gsm basis weight.

15

Table 10. Medium Uptake Pressure, Medium Desorption Pressure, and Caliper.

Product	MUP (g/g)	MDP (cm)	Caliper (mm)
XLA	1.00 (11.3)	1.00 (21.6)	1.00 (2.7)
XLB	1.15	0.79	1.50
EXPRO-D	1.20	0.83	2.10
EXPRO-E	1.50	0.55	3.06
EXPRO-F	1.52	0.356	4.44

20       The acquisition rate, and rewet, and tensile strength of representative products of the invention were determined and compared to conventional airlaid webs. The normalized results are presented in Table 11. In Table 11, XLA refers to an airlaid web of cellulosic fibers crosslinked with citric acid; XLB refers to an airlaid web of cellulosic fibers crosslinked with a combination of citric and polyacrylic acid fibers; EXPRO-D refers to a foam-formed composite of cellulosic fibers crosslinked with

25

citric acid; and EXPRO-E refers to a product of the invention formed from cellulosic fibers treated with citric acid. All samples tested at 300 gsm basis weight.

Table 11. Acquisition Rate, Rewet, and Tensile Strength.

5

Product	Acquisition Rate (ml/sec)	Rewet (g)	Tensile Strength (g/in)
XLA	1.00 (0.44)	1.00 (0.87)	0
XLB	1.50	0.75	0
EXPRO-D	2.00	0.75	1000
EXPRO-E	2.64	0.58	1350

While the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the spirit and scope of the invention.